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NEW LIQUID CATHODES FOR LITHIUM BATTERIES PART A
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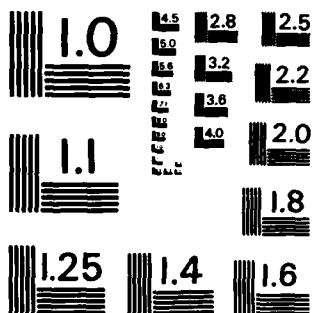
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NEW LIQUID CATHODES FOR LITHIUM BATTERIES PART A. HALOCARBONS

BY KATHLEEN M. O'NEILL, STANLEY D. JAMES,
PATRICIA H. SMITH

RESEARCH AND TECHNOLOGY DEPARTMENT

MAY 1984

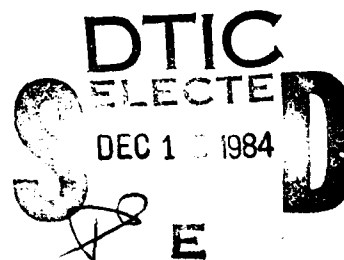
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FOREWORD

This study has surveyed a wide range of commercially available organic liquids to investigate their usefulness as safe and efficient cathode materials for lithium batteries. A qualitative assessment of the chemical stability of lithium metal with halocarbon electrolytes indicated that several were sufficiently stable for continued characterization. Further testing comprised: shock sensitivity with lithium, conductivity of halocarbon electrolytes, and the discharge behavior of assembled Li battery packs at 1mAcm^{-2} .

Halocarbons were found to be much less shock sensitive with lithium than presently used sulfur oxychlorides. A literature search has revealed that they are also less toxic. The discharge capacity for 1,1,2,2-tetrachloroethane (2.8 AH/g carbon) exceeded that of thionyl chloride (2.2 AH/g carbon). These results show promise for the use of halocarbons in safer lithium batteries.

The authors acknowledge Mr. A. E. Webb of the Metrology Branch at NSWC for his help with discharge equipment.

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Approved by:

J. R. Dixon

JACK R. DIXON, Head
Materials Division



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CHAPTER 1

INTRODUCTION

Lithium is the most electronegative and low molecular weight metal, making it an excellent candidate for anode material. Two present lithium systems, Li/SOCl_2 and Li/SO_2 , have proven to be successful in yielding high energy density with excellent discharge characteristics. However, after 10 years of research and development, safety problems persist in these systems. Under some conditions they are prone to fires and explosions with the venting of toxic gases. The objective of this study is to investigate various alternatives to current lithium systems that are safer without sacrificing too much of their high energy density.

CHAPTER 2

EXPERIMENTAL

MATERIAL SCREENING

A study was performed to make a qualitative assessment of the stability of lithium metal with selected halocarbons and halocarbon electrolytes. This was done by placing 3 mL of the halocarbon (used as received from the manufacturer) with a 2 gram strip of lithium foil (Foote Mineral Company) in a Teflon-lined, screw cap Pyrex tube at a room temperature of $24 \pm 1^\circ\text{C}$ and sealing with Parafilm. The tubes were observed at intervals of 24 hours; 1, 2, and 3 months. Similar lithium stability tests were performed with 1.0 M LiAsF_6 in a 50 percent by volume mixture of halocarbon and tetrahydrofuran. Identical lithium stability tests with both the pure halocarbon and the electrolyte solutions were done at $50.0 \pm .1^\circ\text{C}$ using a Fisher Isotemp dry bath (Model 145) and monitored with a mercury thermometer traceable to National Bureau of Standards.

The following reagents were used:

tetrahydrofuran (THF), "certified ACS," 1,2-dichloroethane, "certified ACS," Fisher Scientific

LiAsF_6 , Electrochemical Grade, U.S. Steel Agri-chemicals, Decatur, GA

dichloromethane, 98 percent; chloroform, 98 percent; carbon tetrachloride, 99 percent, J. T. Baker Chemical Co.

1,2-dichloropropane, 99 percent; 1,3-dichloropropane, 99 percent; 1,2,3-trichloropropane, 99+ percent; 1,1,2,2-tetrachloroethane, 98 percent; 1-chloropropane, 99 percent; 2-chloropropane, 99 percent; 2-chloro-2-methylpropane, 99 percent, Aldrich Chemical Co.

1,2-dichloro-1,1-difluoroethane, 99 percent; PCR Inc.

thionyl chloride, doubly-distilled, Apache Chemicals, Seward, Ill.

1.5M LiAlCl_4 in SOCl_2 , <5ppm Fe, Lithium Corp. of America, Bessemer City, NC

sulfuryl chloride, 99 percent, Alfa Chemicals.

SHOCK SENSITIVITY TESTING

The technique for shock sensitivity testing used at the Naval Surface Weapons Center is a modification of that developed at the Explosives Research Laboratory (ERL) in Bruceton, PA.^{1,2} The sample tube consisted of a flame sealed 4 mm O.D. Pyrex tube stoppered with a Viton rubber closure containing 12±1 mg of lithium and approximately 100 microliters of the liquid to be tested. Sample tubes were placed in the ERL Drop Weight Impact Tester under a 0.5 kg striker and a 2.5 or 5.0 kg weight was dropped on the sample from set heights. An explosion was determined to occur if a certain decibel level was exceeded on a noise meter. The run was conducted and reduced to the height for 50 percent explosability by the "up and down method" described by Dixon and Massey.³

CONDUCTIVITY

Conductivity measurements were carried out using a Yellow Springs Instrument borosilicate dip-type cell (Model #3403) requiring 5 ml of sample. The platinum electrodes of this cell were platinized and the cell constant was determined as 1.09 cm⁻¹. All resistance measurements were carried out using a General Radio, type 1650-B impedance bridge at 1000 Hz. Capacitance balance was provided to ensure sharp null points. The bridge measured with an accuracy of + 1.0 percent. Solutions were maintained at 25 ± 0.2°C by means of a Forma Scientific Inc., Model 2095-2 constant temperature bath. Equilibrium temperature of the bath was read on a mercury thermometer (traceable to NBS) with an accuracy ± 0.1°C.

DISCHARGE PROCEDURES

Constant-current discharges of lithium/chlorocarbon couples were performed under argon in a Pyrex research cell using pre-assembled battery packs (Figure 1) as used at Honeywell Power Sources Center, Horsham, PA. In these packs the cathode (normally 0.025"x0.5"x1.0") is Teflon-bonded Shawinigan Black supported on Ni Exmet. This is sandwiched between a Li anode (.020"x0.5"x1.0") and Li reference supported on Ni Exmet. Electrodes were separated by two sheets of 0.005" Manninglas 1400 Mat glass fiber separator paper. The two-plate electrode pack was secured in place by two glass slides and Teflon-coated nickel binding wire. All cells were evacuated at reduced pressures of less than one torr for one hour prior to adding electrolyte under vacuum. Cells were activated by tilting the reaction cell to allow the battery pack to wet. Only the separator

¹Eyster, E. H., and Smith, L. C., Studies of the ERL Drop Weight Impact Machine at NOL, NOLM-10003, 25 Jan 1949.

²Mallory, H. O., Ed., The Development of Impact Sensitivity Testing at the Explosives Research Laboratory, Bruceton, PA, During the Years 1942-45, NAVORD Report 4236, 16 Mar 1956.

³Dixon W. J., and Massey, F. J., Introduction to Statistical Analysis (New York: McGraw-Hill Book Co., Inc., 1951), Chapter 19.

paper protruding from the bottom of the battery pack was immersed in the electrolyte during cell discharge. This procedure has been shown at Honeywell to yield discharge efficiency data that reliably reflects the behavior of commercial, jelly rolled cells.⁴ Flooded electrodes can yield misleadingly high discharge times due to dissolution of discharge products. All experiments were duplicated and in most cases, the results are reproducible. Discharge was normally terminated when the voltage of the cathode versus the reference electrode fell below +0.8V or when the voltage of the anode versus the reference electrode equaled the cathode voltage.

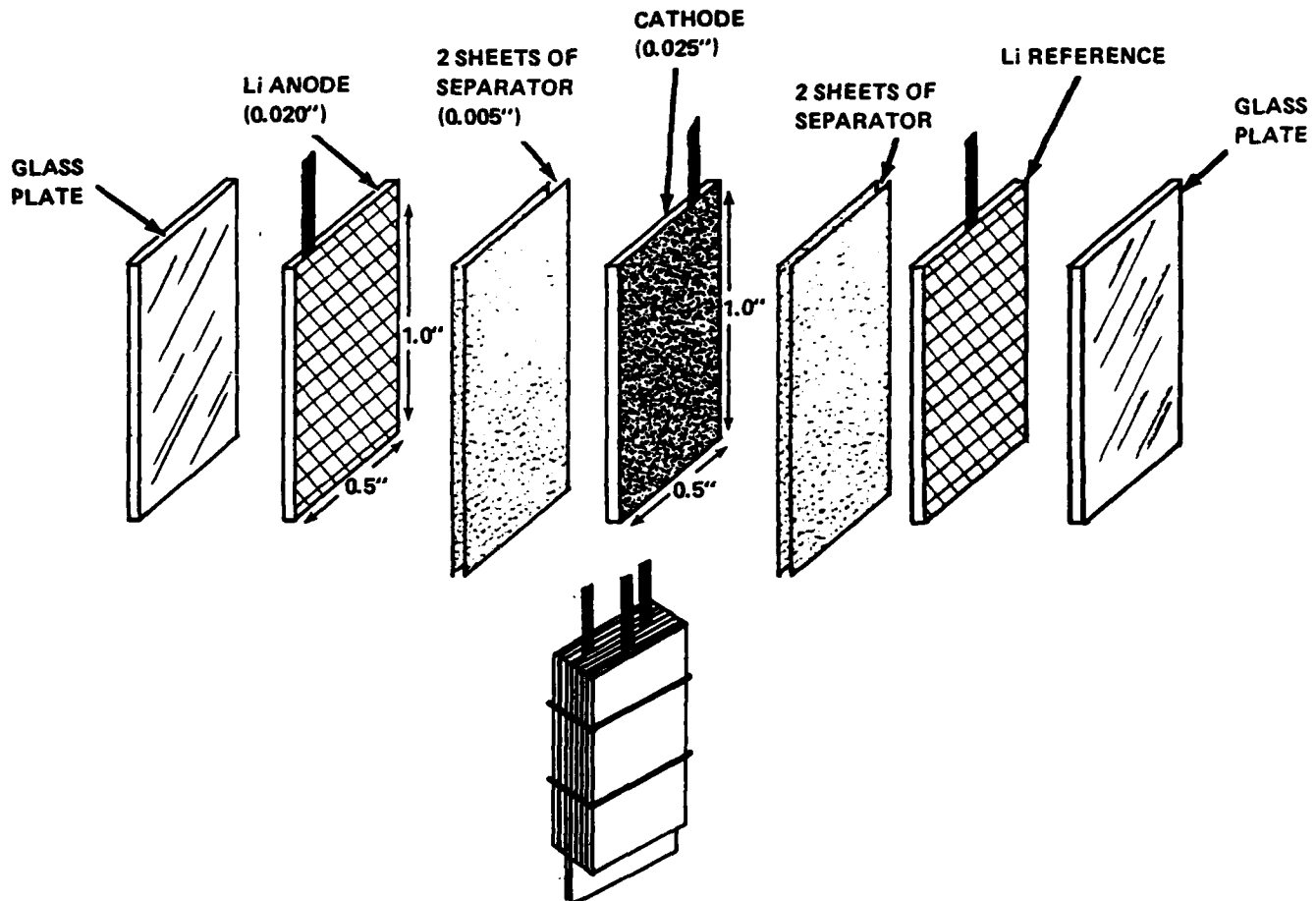


FIGURE 1. SCHEMATIC DIAGRAM OF PRE-ASSEMBLED BATTERY PACKS

⁴Doddapaneni, N., High Efficiency Lithium-Thionyl Chloride Cell, Final Report (4-10-81 to 5-9-82) DELET-TR-81-0381-F, Aug 1982.

CHAPTER 3

RESULTS AND DISCUSSION

MATERIAL SCREENING

The results of the initial halocarbon screening are shown in Table 1. The six chlorocarbons selected for further study because of their stability at 24°C were tested at 50°C also. Lithium stability was assessed with pure halocarbon (column 3) and with electrolyte solutions of 50 percent halocarbon/50 percent THF; 1M LiAsF₆ (column 4) using the following qualitative scale:

- A. retained shiny metallic appearance
- B. mottled black
- C. thin black film
- D. thick, dark, black film
- E. white film
- F. pitted surface
- G. reacted completely

Liquid stability (halocarbon or halocarbon electrolyte) was similarly assessed:

- 1. clear and colorless
- 2. yellow tint
- 3. yellow
- 4. red

The black films (B-D) formed on lithium with some of the halocarbon are attributed to the final reduction product carbon ($x + y\text{Li} + \text{CF}_x\text{Cl}_y \rightarrow x\text{LiF} + y\text{LiCl} + \text{C}$) and do not affect the Li integrity. In the case of F and G the lithium is pitted or reacted. This eliminated several compounds from consideration. Halocarbons selected for discharging were tested at 24°C and 50°C. The high temperature testing appeared to accelerate the formation of the black films.

Lithium can react with various organic halides to produce alkyl lithium compounds. For example: $\text{CH}_3\text{Br} + 2 \text{Li} \xrightarrow{\text{ether}} \text{CH}_3\text{Li} + \text{LiBr}$. Ethers such as diethyl ether or tetrahydrofuran provide an inert, slightly polar medium in which organometallics are usually stable. The reactivity order of the various halides has been shown to increase in the order: $\text{I} > \text{Br} > \text{Cl} \gg \text{F}$.⁵ The few iodine and bromine compounds tested proved reactive in the electrolyte

⁵Morrison, R. T., and Boyd, R. N., Organic Chemistry (Boston: Allyn and Bacon, Inc., 1973), p. 93.

TABLE 1. CHEMICAL STABILITY OF LITHIUM WITH HALOCARBONS

HALOCARBON	TEMP C	PURE HALOCARBON				ELECTROLYTE SOLUTION*			
		24 hrs	1 mo	2 mo	3 mo	24 hrs	1 mo	2 mo	3 mo
Cl-C-Cl	24° 50°	B1 B1	→	→	→	A1 A1	→	B1	→
$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{Cl} \end{array}$	24°	E1	→	→	→	A1	→	→	→
CCl ₄	24°	B1	→	→	→	G4	→	→	→
Cl-C-C-Cl	24° 50°	B1 B1	→	→	→	A1 A1	→	→	→
$\begin{array}{cc} \text{Cl} & \text{Cl} \\ & \\ \text{Cl}-\text{C}-\text{C}-\text{Cl} \end{array}$	24° 50°	B1 C1	→	C1	→	A1 A1	→	→	A2 G3
$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-\text{C} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	24° 50°	A1 A1	→	B1 B1	→	A1 A1	→	→	→
$\begin{array}{cc} \text{C} & \text{C} \\ & \\ \text{Br} & \text{Br} \end{array}$	24°	A1	→	C2	→	G3	→	→	→
$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-\text{C} \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$	24°	C1	→	→	→	F3	→	→	→
$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-\text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array}$	24°	C1	→	D2	→	A1	→	E4	→
Cl-C-C-C	24°	G3	→	→	→	G3	→	→	→
$\begin{array}{c} \text{C}-\text{C}-\text{C} \\ \\ \text{Cl} \end{array}$	24°	G1	→	→	→	G3	→	→	→
$\begin{array}{c} \text{C}-\text{C}-\text{C} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	24° 50°	D1 C1	→	→	C2	→	A1 A1	→	B2
$\begin{array}{c} \text{C}-\text{C}-\text{C} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	24° 50°	B1 B1	→	→	C1	→	A1 A1	→	F3
$\begin{array}{ccc} \text{C} & -\text{C}- & \text{C} \\ & & \\ \text{Cl} & & \text{Cl} \end{array}$	24° 50°	B2 B2	→	→	G4 G4	→	A1 A1	→	G4
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{Cl} \end{array}$	24°	B1	→	→	→	E2	→	→	→
$\begin{array}{ccc} \text{Cl} & & \text{Cl} \\ & & \\ \text{Cl}-\text{C}-\text{C}-\text{C} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	24°	B1	→	B2	→	G3	→	→	→
$\begin{array}{c} \text{F} \\ \\ \text{C}-\text{C}-\text{C} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	24°	D1	→	D2	→	G4	→	→	→
$\begin{array}{c} \text{C}-\text{C}-\text{C} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	24°	A1	→	E3	→	G1	→	G3	→

QUALITATIVE SCALES

LITHIUM

- A - RETAINED SHINY METALLIC APPEARANCE
 B - MOTTLED BLACK
 C - THIN BLACK FILM
 D - THICK, DARK, BLACK FILM
 E - BLACK FILM WITH WHITE EDGES
 F - PITTED
 G - REACTED COMPLETELY

LIQUID

- 1 - CLEAR AND COLORLESS
 2 - YELLOW TINT
 3 - YELLOW
 4 - RED

*50% THF/50%
 HALOCARBON
 1M LiAsF₆

solution with THF, while the chlorocarbons themselves were stable with Li. Thus, a change of electrolyte might make these compounds usable as high voltage cathode materials. A discharge of 50 percent 2-iodo-1,1,1-trifluoroethane/50 percent THF; 1M LiAsF₆ yielded a plateau voltage of 2.2 but failed prematurely due to anode reactivity. Several halocarbons and their electrolytes were found to be stable with Li for over 3 months of observation even at temperatures of 50°C. Alkyl fluorides are not known to react with Li.⁶

After several hours at room temperature (24°C), carbon tetrachloride (CCl₄) and dichloromethane (CH₂Cl₂) formed mottled black films which remained inert for several months on lithium. Chloroform (CHCl₃) formed a white film with Li after several days. CCl₄ was very reactive in the electrolyte solution. In CHCl₃ and CH₂Cl₂ electrolyte solutions, the Li appeared clean and shiny for three months of observation.

1,2-Dichloroethane, 1,1,2,2-tetrachloroethane, and 1,2-dichloro-1,1-difluoroethane appeared stable towards Li during the study. When in contact with electrolyte solutions of 50 percent chlorocarbon, 50 percent THF, 1.0 M LiAsF₆ the Li maintained its shiny metallic appearance for 3 months. Similar results were obtained at 50°C.

The reactivity of the chlorine substituted propanes varied widely with the number and location of the chlorines. 2-Chloropropane and 1-chloropropane reacted with Li within minutes. 1,2,3-Trichloropropane was slightly less reactive, but showed signs of Li attack after 24 hours. 2-Chloro-2-methylpropane formed a black film on Li which remained unchanged after 3 months. It was very reactive with Li in the electrolyte solution. 1,1,1,3-Tetrachloropropane with Li had yellow liquid discoloration after 1 week at 24°C, but the Li appeared unchanged.

Stability studies with 1,2-dichloropropane and 1,3-dichloropropane detected the appearance of the black films common with Li/halocarbon combinations. The Li appeared stable for 3 months at 24 and 50°C. Electrolyte studies on 1,2-dichloropropane showed the Li unreacted after 3 months at both temperatures. Testing on 1,3-dichloropropane electrolyte showed some reaction at the edges of the Li after two weeks at 50°C. This reaction was not detected after 3 months at 24°C.

The remaining compounds tested, 1,1,1,3-tetrachloropropane, 1,2-dichloro-2-fluoroethane, and 2,3-dichloropropene, were very reactive in the electrolyte solutions of THF and LiAsF₆ at 24°C. The use of other cosolvents could prevent this reactivity.

SHOCK SENSITIVITY

These tests were done to ensure that the chlorocarbons selected for more extensive study were less shock sensitive with lithium than are the sulfur oxychlorides of existing lithium batteries. Thus, if their discharge behavior is found to be acceptable, they may provide safer systems. Shock sensitivity

⁶Morrison, p. 93.

testing is commonly used to evaluate the impact sensitivity of explosives. Its usefulness in testing metal-halogenated solvent combinations was evaluated by the Armed Services Explosives Safety Board in 1968.⁷

The height for 50 percent explodability (Table 2) is an inverse function of its shock sensitivity. The lower the height, the more sensitive a compound is to impact. Both SO_2Cl_2 at only 36 cm and SOCl_2 at 49 cm were discovered to be extremely shock sensitive to Li. These values reflect that the Li-sulfur oxychloride combinations are even more impact sensitive than TNT (160 cm) using the same 2.5 kg drop weight.

In contrast, the halocarbons investigated were substantially less shock sensitive with lithium than SOCl_2 and SO_2Cl_2 . Initial runs using the standard 2.5 kg weight on the chlorocarbons gave no detectable sensitivity at the maximum drop-height of the machine (320 cm). After doubling the weight to 5.0 kg, some sensitivity was detected with 1,1,2,2-tetrachloroethane (173 cm), dichloromethane (194 cm), and 1,2,3-trichloropropane (257 cm). These are 4 to 5 times the height obtained for SOCl_2 and SO_2Cl_2 using the lighter 2.5 kg weight. The other three chlorocarbons still gave no impact sensitivity with Li under the most severe conditions imposed by the machine.

This greatly reduced shock-sensitivity to lithium of chlorocarbons vs. sulfur oxychlorides is highly encouraging for the use of chlorocarbons in safer lithium batteries. It is further noted that the chlorocarbons are also several orders of magnitude less toxic than SO_2 or SOCl_2 during maximum levels of exposure for 30 minutes or for constant levels during a normal work week of 40 hours (Table 3).

CONDUCTIVITY

The solubility of several Li salts (LiAsF_6 , LiAlCl_4 , LiClO_4 , LiBF_4 , LiCl , LiBr) in the chlorocarbons investigated was found to be extremely low. This is a result of the chlorocarbons' low dielectric constant and non-polar properties. However mixtures of 50 percent halocarbon/50 percent THF readily dissolve LiAsF_6 forming 1.0 M solutions with sufficiently high conductivity for investigating cathode performance (Table 4).

The commonly used SOCl_2 electrolyte, 1.5 M in LiAlCl_4 , has a specific conductance of $18.0 \Omega^{-1}\text{cm}^{-1} \times 10^{-3}$ and a molar conductance of $12.0 \Omega^{-1}\text{cm}^2 \text{mol}^{-1}$.⁸ The molar conductance values for the 50 percent chlorocarbon, 50 percent THF (1.0 M LiAsF_6) electrolyte range from $15.7 \Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ for dichloromethane to 5.59 for 1,1,2,2-tetrachloroethane. The discharges were performed at a concentration of 1.0 M LiAsF_6 . It has been shown that the opposing effects of increasing charge

⁷Armed Services Explosives Safety Board, Abstracts 7-67 through 6-68, Potential Incident #39 (1968).

⁸Dey, A. N., "Primary Li/ SOCl_2 Cells. X. Optimization of D Cells With Respect To Energy Density, Storability and Safety," J. Power Sources, Vol. 5, 1980, p. 57.

TABLE 2. RELATIVE SHOCK SENSITIVITIES OF Li/CHLOROCARBON COMBINATIONS (12 mg Li AND 100 μ L LIQUID)

CHLOROCARBON	MASS OF DROP-WEIGHT USED, KG	50%H,cm*	STD. DEV. σ ,cm
1,2-dichloropropane	5.0	>320	-
	2.5	>320	-
1,3-dichloropropane	5.0	>320	-
	2.5	>320	-
1,2-dichloroethane	5.0	>320	-
	2.5	>320	-
1,2,3-trichloropropane	5.0	257.4	0.05
	2.5	>320	-
dichloromethane	5.0	194.3	0.09
	2.5	>320	-
1,1,2,2-tetrachloroethane	5.0	173.2	0.11
	2.5	>320	-
thionyl chloride	2.5	48.8	0.07
sulfuryl chloride	2.5	35.9	0.17

*Height for 50% explodability, i.e., 50% of the samples impacted from this drop-height will explode on average.

TABLE 3. TOXICITY DATA FOR CATHODE MATERIALS

<u>Compound</u>	<u>IDLH*</u> <u>(ppm)</u>	<u>TLV**</u> <u>(ppm)</u>
dichloromethane	5,000	500
1,2-dichloroethane	1,000	50
1,2-dichloropropane	2,000	75
1,3-dichloropropane	1,000	--
1,2,3-trichloropropane	1,000	50
1,1,2,2-tetrachloroethane	150	5
tetrahydrofuran	20,000	200
sulfur dioxide	100	2
thionyl chloride	--	1

*IDLH (immediately dangerous to life or health) - maximum level without irreversible health effects of 30 minutes duration. NIOSH/OSHA Guide to Chemical Hazards, HEW, DOC, 1978

**TLV-TWA (threshold limit value - time weighted average) - repeated exposure 8 hrs, day; 40 hrs a week without adverse affect. Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1982.

TABLE 4. CONDUCTIVITY DATA FOR 1.0 M LiAsF_6 ELECTROLYTE SOLUTIONS
OF 50 PERCENT CHLOROCARBON/50 PERCENT THF AT 25°C

CHLOROCARBON	CONDUCTANCE	
	SPECIFIC, κ $\Omega^{-1}\text{cm}^{-1} \times 10^3$	MOLAR, λ $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
dichloromethane	15.7	15.7
1,2-dichloroethane	12.9	12.9
1,3-dichloropropane	10.4	10.4
1,2-dichloropropane	9.71	9.71
1,2,3-trichloropropane	6.37	6.37
1,1,2,2-tetrachloroethane	5.59	5.59
thionyl chloride (1.5M LiAlCl_4)	18.0	12.0

carriers and viscosity tend to balance at a conductivity maximum of approximately one molar.⁹ Future investigations will be directed toward optimizing the chosen system by varying the cosolvent and salt composition and concentration. Further purification of reagents may also result in increased battery performance.

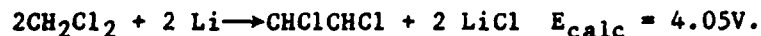
DISCHARGE BEHAVIOR

Table 5 summarizes the discharge characteristic of selected Li/chlorocarbon couples compared to thionyl chloride. Capacities were taken to a 0.8V cut off (Cathode vs Li reference) in those cases attributed to cathode failure (Figures 2-6) or when $V_{\text{anode}} = V_{\text{cathode}}$ (Figure 7) in the case of anode failure.

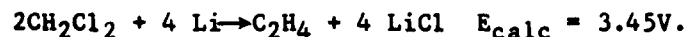
The cells discharged at 1mAcm^{-2} from an initial OCV of 3.18 - 3.11V for 30 to 45 minutes before reaching a steady state plateau voltage. 1,1,2,2-Tetrachloroethane (Figure 2) was shown to give the highest working voltage (1.6V). The cathode plateau is very flat until the end of discharge where it slopes gently due to cathode failure. The anode is relatively flat at less than 0.1V vs the Li reference until the end of discharge where it mimics the failure of the cathode. This system also had the greatest capacity, averaging 2.8 AH per gram of Shawinigan carbon black in the cathode. Discharges of thionyl chloride using identical cell packs gave an average capacity of 2.2 AH/g carbon under the same conditions. It is noted that of the six halocarbons under investigation, this system has the greatest number of potentially reducible chlorides. At the present time no trend has been observed correlating number of reducible halogens to cathode capacity.

The other halocarbons tested are listed in descending order of performance in Table 5. 1,2-Dichloroethane has an average capacity of 2.0 AH/g carbon. Its discharge curve (Figure 3) has a slightly greater slope than 1,1,2,2-tetrachloroethane (Figure 2) and a working voltage of 1.4. Both 1,2-dichloropropane (Figure 4) and 1,3-dichloropropane (Figure 5) have very similar capacities within experimental error of 1.6 and 1.5 AH/g carbon respectively. This can be attributed to their similar structures and reduction pathways. Dichloromethane (Figure 6) exhibited a sloping voltage plateau from 1.5 to 1.0V and a relatively low capacity of .9 AH/g carbon. The lowest capacity (.65 AH/g carbon) was obtained by 1,2,3-trichloropropane (Figure 7). Failure analysis showed the anode was severely pitted and coated with an orange film. This was caused by a direct chemical reaction between the Li and the chlorocarbon.

Theoretical voltage calculations for the reduction of halocarbons indicate that working voltages from 3-4V are expected. For example, a one electron per molecule reduction of dichloromethane has a theoretical voltage of 4.05,



A two electron per molecule reduction has a theoretical voltage of 3.45V,



⁹Besenhard, J. O., and Eichinger, G., "High Energy Density Lithium Cells Part I. Electrolytes and Anodes," J. Electroanal. Chem., Vol. 68, 1976, p. 8.

TABLE 5. SUMMARY OF PERFORMANCE DATA FOR LITHIUM/50 PERCENT CHLOROCARBON, 50 PERCENT THF
(1.0 M LiAsF₆)/SHAWINIGAN BLACK CELLS

CATHODE	OCV	DISCHARGE TIME (HRS)	FAILURE A/C ^a	PLATEAU VOLTAGE	AH AT CELL FAILURE ^{a,b}	CAPACITY AH/g CARBON
1,1,2,2-tetrachloroethane CHCl ₂ CHCl ₂	3.18 3.17 3.18	46.0 37.8 57.0	C C C	1.6-1.4 1.6-1.4 1.6-1.4	.148 .122 .184	3.39 2.79 2.24
1,2-dichloroethane CH ₂ ClCH ₂ Cl	3.13 3.15	54.0 53.9	C C	1.4-1.3 1.4-1.3	.176 .174	2.05 2.02
1,2-dichloropropane CH ₂ ClCHClCH ₃	3.16 3.16 3.15	48.4 38.9 40.5	C C C	1.4-1.2 1.4-1.2 1.4-1.2	.156 .125 .130	1.82 1.46 1.52
1,3-dichloropropane CH ₂ ClCH ₂ CH ₂ Cl	3.15 3.15 3.14	48.6 34.0 36.0	C C C	1.4-1.2 1.4-1.2 1.4-1.2	.156 .109 .116	1.82 1.28 1.35
dichloromethane CH ₂ Cl ₂	3.13 3.13	28.8 20.8	C C	1.5-1.0 1.5-1.0	.0927 .0670	1.08 .780
1,2,3-trichloropropane CH ₂ ClCHClCH ₂ Cl	3.13 3.11	15.8 18.5	Ab Ab	1.3 1.3	.0509 .0596	.593 .694
thionyl chloride SOCl ₂	3.65 3.62 3.63	35.5 32.3 27.3	C C C	3.4 3.4 3.4	.114 .104 .0879	2.45 2.24 2.01

^aCell failure attributed to cathode when V cathode vs V reference = 0.8V^bCell failure occurred when V anode = V cathode

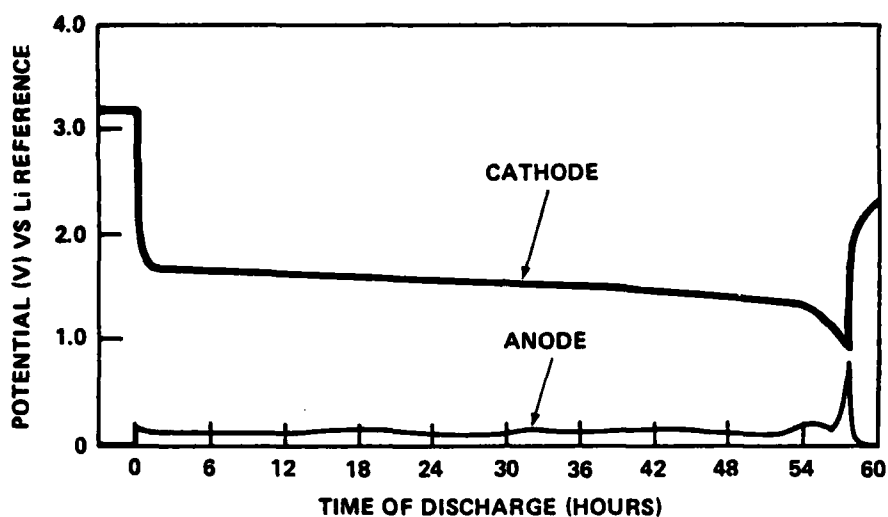


FIGURE 2. DISCHARGE CURVE FOR 50% 1,1,2,2 - TETRACHLOROETHANE/
50% THF VERSUS Li ANODE (1M LiAsF₆, 1mA · cm⁻², 24°C)

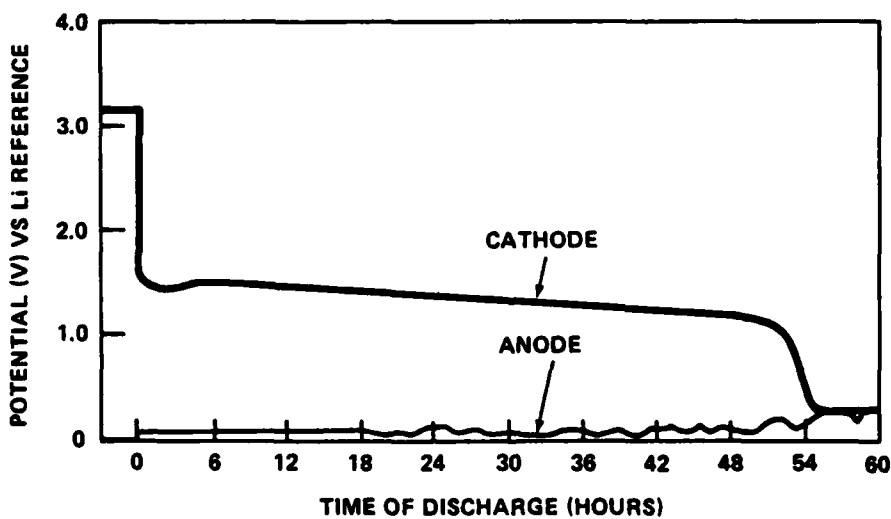


FIGURE 3. DISCHARGE CURVE FOR 50% 1,2 - DICHLOROETHANE/
50% THF VERSUS Li ANODE (1M LiAsF₆, 1 mA · cm⁻², 24°C)

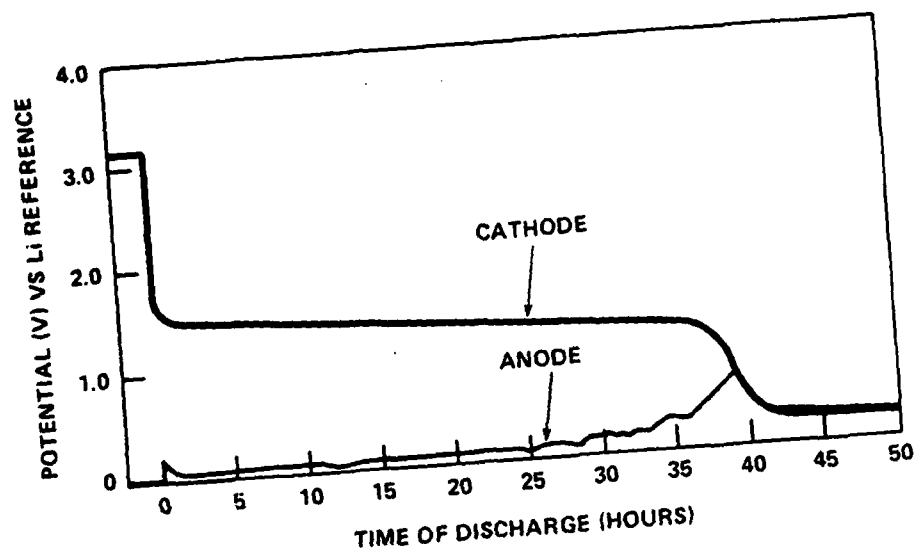


FIGURE 4. DISCHARGE CURVE FOR 50% 1,2 - DICHLOROPROPANE/
50% THF VERSUS LI ANODE (1M LiAsF₆, 1 mA · cm⁻², 24°C)

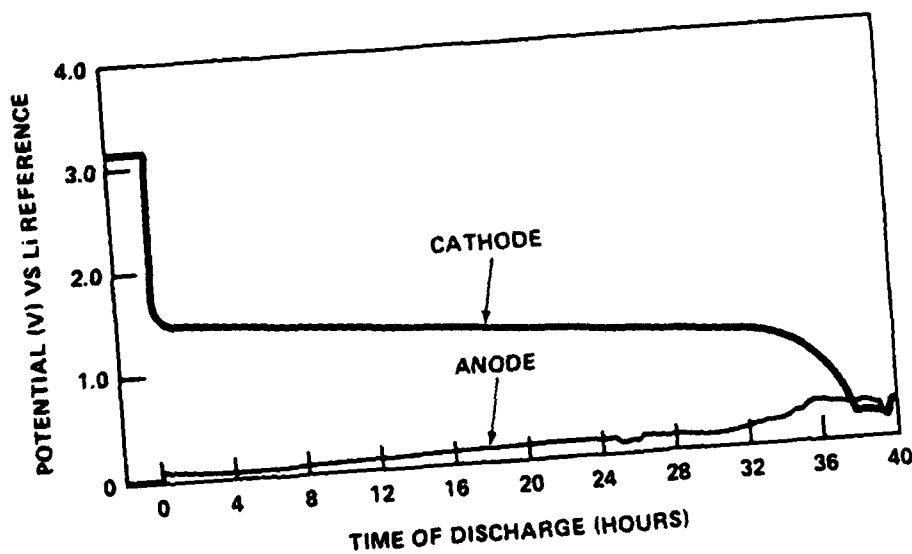


FIGURE 5. DISCHARGE CURVE FOR 50% 1,3 - DICHLOROPROPANE/
50% THF VERSUS LI ANODE (1M LiAsF₆, 1 mA · cm⁻², 24°C)

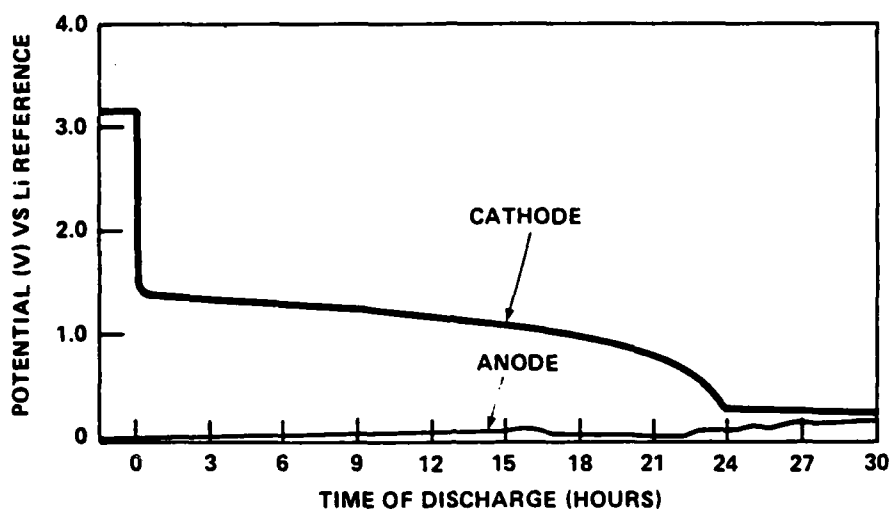


FIGURE 6. DISCHARGE CURVE FOR 50% DICHLOROMETHANE/
50% THF VERSUS Li ANODE (1M LiAsF₆, 1 mA · cm⁻², 24°C)

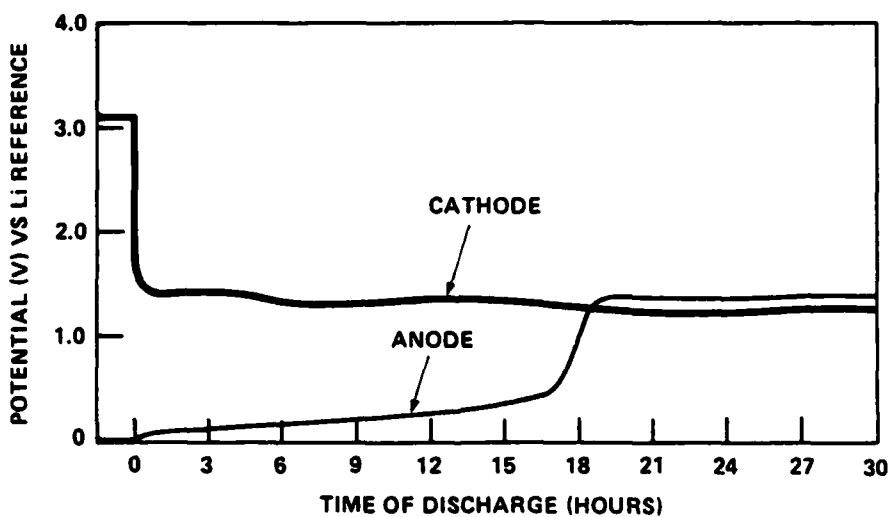


FIGURE 7. DISCHARGE CURVE FOR 50% 1,2,3 - TRICHLOROPROPANE/
50% THF VERSUS Li ANODE (1M LiAsF₆, 1 mA · cm⁻², 24°C)

However, as shown in Table 5, the experimental working voltages for these cells are in the range of 1.6 to 1.4V. This implicates cathode polarization which points to the need for electrocatalysis. Future work will be directed toward looking at several catalysts such as Pd and Ni metal and Ni complexes. A literature search has revealed that these compounds are excellent catalysts for the chemical reduction of halocarbons.¹⁰

¹⁰Feast, W. J., Musgrave, W. K. R., Coffey, S., Ed., Rodd's Chemistry of Carbon Compounds (New York: Elsevier Publishing Co., 1964), Vol. 1, p. 256-257.

CHAPTER 4

CONCLUSIONS

Table 6 is a comparison between the best present experimental cell surveyed, and typical primary batteries. The starred values for 1,1,2,2-tetrachloroethane are estimates of cell performance calculated by taking the ratio of experimentally measured AH/g of carbon for the halocarbons and SOCl_2 from Table 5 and multiplying by the AH/lb of a typical commercial Li/ SOCl_2 battery. Implicit in this calculation is the assumption that the construction of a Li-halocarbon battery will not differ significantly from that of a Li/ SOCl_2 battery apart from the relatively minor difference of electrolyte weights. 1,1,2,2-Tetrachloroethane has a capacity of 99 AH/lb. This is superior to other common primary batteries such as the common dry, alkaline dry, mercury, and magnesium batteries. Multiplied by its median working voltage of 1.5, this system can produce 149 WH/lb. This value is far superior to non-Lithium systems and is very close to the value for SO_2 cells at 150 WH/lb.

The advantages of halocarbons are summarized:

1. They are several orders of magnitude less toxic than SOCl_2 and SO_2 during maximum exposure levels for 30 minutes and for constant levels during a normal work week of 40 hours. Although they are probably carcinogenic, they are certainly less noxious and less acutely toxic than sulfur oxychlorides. This is an advantage during escape situations in enclosed spaces such as a submarine.
2. The halocarbons have little if any shock sensitivity to Li, whereas the sulfur oxychlorides were shown to be violently shock sensitive with Li.
3. They have excellent capacities. For example, 1,1,2,2-tetrachloroethane produced 2.8 AH/g carbon vs 2.2 AH/g carbon for thionyl chloride.
4. They exhibit good voltage regulation.
5. They are stable with Li when pure and as electrolyte solutions, showing no change in Li integrity for over 3 months at temperatures up to 50°C.

These results show promise for the use of halocarbons in safer Lithium batteries.

TABLE 6. COMPARISON OF PRESENT LITHIUM/HALOCARBON CELLS WITH TYPICAL PRIMARY BATTERIES

CELL TYPE	OPEN CIRCUIT VOLTAGE	TYPICAL WORKING VOLTAGE	WATT HOURS/lb	CALCULATED AMP HOURS/lb
COMMON DRY	1.60	0.9-1.4	20-30	23
ALKALINE DRY	1.50	0.9-1.4	30-40	32
MERCURY	1.35	1.3	35-45	31
MAGNESIUM	1.8	1.5-1.6	40-45	27
LITHIUM-SULFUR DIOXIDE	2.9	2.7-2.8	150	55
LITHIUM-THIONYL CHLORIDE	3.6	3.4-3.5	300	87
1, 1, 2, 2-TETRACHLOROETHANE	3.18	1.4-1.6	149*	99*

* BASED ON THE ASSUMPTION THAT CELL CONSTRUCTION WOULD BE SIMILAR TO THE Li-SOCl_2 BATTERY

$$\text{CALCULATED AH/lb} = \frac{\text{AH/g C FOR HALOCARBON}}{\text{AH/g C FOR SOCl}_2} \times \text{AH/lb FOR TYPICAL Li-SOCl}_2 \text{ BATTERY}$$

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